REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0705-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
970228

3. REPORT TYPE AND DATES COVERED
Technical Reports 1-7, Dec '95-Nov '96

4. TITLE AND SUBTITLE
Synthesis of Ceramics from Solutions: Fuctionally Graded Composites,
NanoComposites and Single Crystal Thin Films

5. FUNDING NUMBERS
AFOSR
F49620-96-1-0003

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8. PERFORMING ORGANIZATION REPORT NUMBER

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10. SPONSORING/MONITORING AGENCY REPORT NUMBER

19970313 012

11. SUPPLEMENTARY NOTES

12A. DISTRIBUTION/AVAILABILITY STATEMENT
A

12B. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

This program has emphasized two topics: 1) the crystallization of metastable, solid-solution structures, their partitioning into equilibrium structures and compositions, and the role of the metastable phase and its partitioning on forming unique, nanometer microstructures important to the mechanics of structural ceramics and their composites, and 2) the formation of single crystal thin films via spin coating single crystal substrates with solution precursors. Results for the first topic are new, namely, the discovery that diffusion limited crystallization concepts used in rapid solidification directly applies to precursors that crystallize at low temperatures during heating. This discovery is significant because solid-solutions can be greatly extended relative to high temperature synthesis and processing routes where equilibrium conditions are rapidly achieved and solid-solutions can be severely limited. Extension of solid-solution fields (and thus defect chemistries) in compositional space is important to synthesize new materials with optical and electronic properties controlled by defect chemistry and/or metastable compositions. Results for the second topic have shown that single crystal thin films can be formed on single crystal substrates with spin-on liquid precursors despite large differences in lattice parameters and/or crystal structures. Several mechanisms have been identified for the growth of single crystal thin films which are very different to the well know vapor phase epitaxy mechanisms. The significance of the second topic is that single crystal (or poly-variant single crystal) thin films of nearly any inorganic material can be produced on any non-reactive (thermodynamically or kinetically) single crystal substrate, despite crystal structure differences between the film and substrate materials. Processing of multi-layer and/or embedded strip line architectures are possible using liquid precursor spin-on techniques for new device technologies.

14. SUBJECT TERMS
Epitaxy, Phase Selection, Solution Synthesis, Ceramics

15. NUMBER OF PAGES
5

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT

Synthesis of Ceramics From Solutions: Functionally Graded Composites, NanoComposites and Single Crystal Thin Films

Contract AFOSR F49620-96-1-0003

Technical Reports 1 through 7

with a Technical Summary

period: December 1995 - November 1996

February 1997

From

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1. Background

This program has emphasized two topics: 1) the crystallization of metastable, solid-solution structures, their partitioning into equilibrium structures and compositions, and the role of the metastable phase and its partitioning on forming unique, nanometer microstructures important to the mechanics of structural ceramics and their composites, and 2) the formation of single crystal thin films via spin coating single crystal substrates with solution precursors. Results for the first topic are new, namely, the discovery that diffusion limited crystallization concepts used in rapid solidification directly applies to precursors that crystallize at low temperatures during heating. This discovery is significant because solid-solutions can be greatly extended relative to high temperature synthesis and processing routes where equilibrium conditions are rapidly achieved and solid-solutions can be severely limited. Extension of solid-solution fields (and thus defect chemistries) in compositional space is important to synthesize new materials with optical and electronic properties controlled by defect chemistry and/or metastable compositions. Results for the second topic have shown that single crystal thin films can be formed on single crystal substrates with spin-on liquid precursors despite large differences in lattice parameters and/or crystal structures. Several mechanisms have been identified for the growth of single crystal thin films which are very different to the well know vapor phase epitaxy mechanisms. The significance of the second topic is that single crystal (or poly-variant single crystal) thin films of nearly any inorganic material can be produced on any non-reactive (thermodynamically or kinetically) single crystal substrate, despite crystal structure differences between the film and substrate materials. Processing of multi-layer and/or embedded strip line architectures are possible using liquid precursor spin-on techniques for new device technologies.

2. Summary of Research

2.1 Metastability of the Fluorite, Pyrochlore and Perovskite Structures in the PbO-ZrO_2-TiO_2 System, Andrew D. Polli, Fred F. Lange, and Carlos G. Levi

Technical Report No. 1

Abstract: The crystallization, transformation, and partitioning of amorphous PbO-ZrO_2-TiO_2 powders produced by pyrolytic decomposition of mixed alkoxide precursors were investigated. Materials have the general formulation $Pb_{1+\chi}Ti_{[1/(1+\phi)]}Zr_{[\phi/(1+\phi)]}O_{3+\chi}$, where $-0.2 \leq \chi \leq 0.2$ is the fraction PbO excess/deficiency and $0 \leq \phi \leq 1$ is the Zr/Ti molar ratio. Most compositions first crystallized as a metastable fluorite structure with varying degrees of pyrochlore-like cation ordering, which transformed to a single perovskite phase upon additional heat treatment. Higher Zr/Ti ratios enhanced the retention of fluorite and reduced the incidence of cation ordering. Compositions with off-stoichiometric amounts of PbO often yielded extended solid solutions prior to partitioning. For example, metastable perovskites with as much as 20% PbO deficiency ($\chi = -0.2$) could be prepared for $0 \leq \phi \leq 1$, but only ~10% PbO excess could be incorporated in solution for $0.33 \leq \phi \leq 1$. Increasing PbO content was found to promote crystallization, suggesting that this oxide acts as a network modifier enhancing mobility within the initial amorphous precursor powder. Higher PbO was also noted to favor cation ordering in the metastable phase and to accelerate the transformation to perovskite, as well as to promote partitioning for hyperstoichiometric compositions. The findings are discussed in light of structural relationships between the fluorite, pyrochlore and perovskite phases, as well as current understanding of the thermodynamics of the system.

2.2 Epitaxial Growth and Structure of Highly Mismatched Oxide Films with Rock-Salt Structure on MgO, P.A. Langjahr, T. Wagner, F.F. Lange, and M. Rühle

Technical Report No. 2

Abstract: CaO thin films were grown on (001) MgO single crystal substrates by a chemical solution deposition method to study the influence of a relatively high lattice mismatch (14%) on the epitaxial growth. In order to minimize an influence of a different crystal structure and chemistry between film and substrate, film and substrate were chosen to have the same structure (NaCl) and a similar chemistry. The films were heat treated until they broke up into single crystal islands on the MgO substrate. X-ray pole figure analysis and TEM observations of the CaO-films showed that most of the grains had a single out-of-plane orientation (111)CaO $\parallel$ (001)MgO, corresponding to two non-redundant, symmetry related in-plane variants [110](111)CaO $\parallel$ [110](001)MgO and [110](111)CaO $\parallel$ [110](001)MgO. A $\Sigma 7/\Sigma 8$ Near Coincidence Site Lattice (NCSL) model could be constructed for the interface, that suggests good lattice and charge

matching for the observed orientation relations. The mechanisms and energetics leading to the experimentally observed orientation relations are discussed.

2.3 Lattice Mismatch Accommodation in Perovskite Films on Perovskite Substrates, P.A. Langjahr, F.F. Lange, T. Wagner, and M. Rühle

Technical Report No. 3

Abstract: Cubic perovskite films with different compositions were grown on perovskite substrates to investigate the influence of a large lattice mismatch on growth phenomena via the chemical solution deposition method, using toluene solutions of different 2-etyhlhexanoates and neodecanoates. The films were pyrolyzed to crystallize the perovskite of the desired composition and then heated to 1000°C to promote epitaxial grain growth. Pole figures obtained via X-ray diffraction as well as selected area diffraction (SAD) of TEM specimen with lattice mismatches of 2.5% ($SrTi_{0.5}Zr_{0.5}O_3$ on $SrTiO_3$), 5% ($SrZrO_3$ on $SrTiO_3$), 7.4% ($BaZrO_3$ on $SrTiO_3$) and 8.2% ($SrZrO_3$ on $LaAlO_3$) reveal only the epitaxial orientation [100](001) film | | [100](001) substrate. The XRD and TEM results also indicate increasing polycrystallinity with increasing lattice mismatch. High resolution electron microscopy (HREM) of films on $SrTiO_3$ demonstrated that an array of misfit dislocations is present at the interface. The misfit dislocations have line vectors l of a<100>-type and Burgers-vectors **b** of a<010>-type. Dislocation separation distances obtained with HREM and XRD lattice parameter measurements show that the strain energy within the films, due to lattice mismatch, is nearly fully relaxed. The mechanisms of epitaxial growth and dislocation formation are discussed.

2.4 Epitaxial Growth and Structure of Cubic and Pseudocubic Perovskite Films on Perovskite Substrates, P. A. Langjahr, T. Wagner, M. Rühle and F. F. Lange

Technical Report No. 4

Asbstract: Cubic and pseudocubic perovskite films on perovskite substrates are used to study the influence of the lattice mismatch on the epitaxial growth of thin films on substrates of the same structure. For the growth of the films, a metalorganic deposition route (MOD) using 2-ethylhexanoates and neodecanoates as precursors, was developed. The decomposition of the precursors was investigated with thermogravimetric analysis (TGA) and x-ray diffraction (XRD). The films were spin-coated on (001)-oriented $SrTiO_3$- and $LaAlO_3$-substrates, pyrolyzed and afterwards annealed between 600°C and 1200°C. XRD-investigations and conventional transmission electron microscopy (CTEM) show, that epitaxial films with the orientation relationship [100](001) film | | [100](001) substrate can be grown. With XRD, it could be shown, that not only ternary oxide films ($SrZrO_3$, $BaZrO_3$ and $BaCeO_3$), but also perovskite solid soulution films ($SrTi_{0.5}Zr_{0.5}O_3$ and $BaCe_{0.5}Zr_{0.5}O_3$) can be prepared. Strong interdiffusion, detected by a shift of the

film lattice parameter towards the substrate lattice parameter was found in $SrZrO_3$- and $BaZrO_3$-films on $SrTiO_3$, annealed at temperatures above 1050°C. High resolution electron microscopy (HREM) studies of $SrZrO_3$ on $SrTiO_3$ show that a crystalline semicoherent interface with a periodical array of misfit dislocations is present.

2.5 Epitaxial Growth of β-SiC Thin Films on a 6H-SiC Substrate Using the Solution Precursor Method, D. Heimann, T. Wagner, J, Bill, and F. Aldinger

Technical Report No. 5

Abstract: A polyvinylmethylsilane precursor has been used for the epitaxial growth of SiC thin films on 6H-SiC single crystal substrates. The films were prepared by dipping the single crystalline 6H-SiC substrates into the precursor polymer solution with subsequent thermal treatments at different temperatures. Transmission electron microscopy (TEM) was used to characterize the microstructure and chemistry of the different SiC films. At 1100 °C, the film was amorphous and contained substantial oxygen. At 1600 °C, an epitaxial, single crystalline β-SiC film was observed.

2.6 Nano-Meter, Binary Composites Produced from Liquid Precursors via Metastable Phases and Phase Partitioning, F. F. Lange

Technical Report No. 6

Abstract: Chemical routes to synthesize inorganics start with solutions containing different metal-organic molecules that remain well mixed during evaporation to a solid precursor. The solid precursor decomposes and crystallizes during heating. Because decomposition (pyrolysis) occurs at very low temperatures relative to the melting temperature of the inorganic, a large free energy change exists for crystallization. This large free energy change is responsible for two very interesting phenomena. First, the size of the critical nucleus for spontaneous crystallization and growth is very small. Thus the grain size of the initial inorganic material produced during crystallization is ≤ 2 nanometers. Second, crystallization occurs at very low temperatures, i.e., either during or subsequent to pyrolysis. Thus diffusion is very limited, resulting in the crystallization of metastable phases, i.e., phases with unexpected (non-equilibrium) structures and/or phases with a solid-solution that is much greater than found for equilibrium conditions (high temperature heat treatments). With this understanding, nano-crystalline materials can be made that are very stable at high temperatures using the following procedure. The first step is to formulate a precursor composition that would produce at least two phases under equilibrium conditions. During and/or subsequent to pyrolysis, only one, metastable crystalline phase will form; it will have a nanometer grain size. Heating to higher temperatures where long range diffusion can occur will cause the single, metastable phase to partition to its stable phases. Since the second phase(s) partition with a smaller size than the initial metastable phase, a multi-phase composite is produced when the size of each phase can be ≤ 100 nano-meters. This nano composite can be stable at high temperatures because the growth of either phase requires long-range diffusion.

These issues are detailed for three binary systems: t-ZrO_2/c-ZrO_2, ZrO_2/Al_2O_3, and ZrO_2/Fe_2O_3.

2.7 Chemical Solution Routes to Single Crystal Thin Films, F. F. Lange

Technical Report No. 7

Abstract: Epitaxial thin films of inorganic single crystals can be grown on single-crystal substrate through with a variety of different solution chemistries. This review emphasizes chemical solution deposition, in which a solution is used to deposit a layer of precursor molecule that decompose to low-density, polycrystalline films during heating. Ways to control film cracking during deposition and heat treatment and why many precursors synthesize metastable crystalline structures are discussed, and the different mechanisms th convert the polycrystalline film into a single crystal are reviewed. Hydrothermal epitaxy in which single crystal thin films are directly synthesized on templating substrates in a aqueous solution at temperatures < 1500 °C, is also discussed.